

COMPOSITION COEXTRUDABLE WITH PVDF

PVDF (polyvinylidene fluoride) because of its very good
5 weatherability, radiation resistance and chemical
resistance is used to protect articles or materials. In
addition, it is appreciated for its glossy appearance
and its resistance to graffiti. This has therefore led
all kinds of substrates to be coated with a PVDF film.
10 However, PVDF adheres very poorly to most substrates
and it is therefore necessary to place an adhesive
composition between the PVDF and the substrate. The
present invention relates to this composition.

15 Advantageously, this composition is coextruded with the
PVDF in order to form a two-layer film, and then this
film is attached to the substrate, for example by hot
pressing. The two-layer film may also be placed in a
mould, the PVDF layer being placed against the wall of
20 the mould, and then the substrate may be injected in
the melt state into the mould. It is also possible,
depending on the nature of the substrate, to coextrude
the PVDF, the adhesive composition and the substrate in
order to obtain the PVDF-coated substrate directly,
25 with the adhesive composition being between the PVDF
and the substrate.

Patent GB 1 578 517 describes an ABS coated with a PVDF
film, a polyurethane layer possibly being placed
30 between the PVDF and the ABS.

Patent US 4 226 904 describes a PMMA covered with a
PVDF film. To improve the adhesion, a PMMA solution in
dimethylformamide is deposited on the PVDF film and,
35 after the solvent has evaporated, the PVDF film is
pressed onto the PMMA.

Patent US 4 415 519 describes an ABS or PVC substrate
covered with a PVDF film, an adhesive being placed
between the PVDF and the substrate. This adhesive may
40 be either PMMA or a blend of 40% PMMA, 30% PVDF, and

30% ABS by weight, or else a blend consisting of 30% PMMA, 40% of a polyacrylic derivative and 30% ABS by weight.

5 Patent US 4 364 886 describes an ABS or unsaturated polyester substrate covered with a PVDF film, an adhesive being placed between the PVDF and the substrate. This adhesive is a blend of 30% PMMA, 40% of an acrylic elastomer and 30% ABS by weight.

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Patent US 5 242 976 describes a composition coextrudable with PVDF in order to make it adhere to substrates. The composition is a blend of 27 to 50% PMMA, 17.5 to 36.5% PVDF and 25 to 47.45% of an acrylic elastomer by weight.

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In all the above documents of the prior art, there is no mentioned of UV stabilisers in the adhesive composition.

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Patent EP 733 475 B1 describes PVDF-coated substrates; the structure comprises, in succession, the substrate, an adhesive layer, a PVDF layer made opaque to UV and to visible radiation and a PVDF layer. The opaque PVDF layer is obtained by adding a product chosen from metal oxides, pigments and benzophenones to the PVDF. The examples illustrate only PVDF filled with 15% by weight of zinc oxide.

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30 Patent US 5 256 472 describes two-layer films comprising a first layer essentially consisting of PVDF and of a minor amount of PMMA and a second layer intended to ensure adhesion to a substrate. This adhesive layer consists by weight of 50 to 95 (preferably 70 to 90) parts of PMMA, 5 to 50 (preferably 10 to 30) parts of PVDF and 0.1 to 15 parts of a UV absorber. It is explained that the presence of the UV absorber is necessary because this adhesive layer is sensitive to radiation and that if no UV absorber is included then the adhesive is destroyed and

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the layer essentially consisting of PVDF debonds from the substrate. The term "PMMA" denotes methyl methacrylate homopolymers or methyl methacrylate copolymers with a copolymerisable monomer and also blends with an acrylate rubber, but without specifying the proportions of PMMA and of rubber. It is also specified that if the proportion of PMMA is less than 50 parts, the dispersion of the UV absorber tends to be inadequate and evaporation or dissipation of the UV absorber is likely to take place, such being undesirable (column 4, lines 25-29). In addition, it has been discovered that this exudation of absorber impairs the transparency of the films and above all causes debonding. In addition, these films have no mechanical strength, making them difficult to handle. It is therefore necessary for the adhesive layer to contain an elastomer; and, according to the teaching of US 5 242 976 already mentioned, this proportion must be between 25 and 47.45% as calculated from the minimum and maximum values set forth in the abstract and column 2, lines 6-14.

A composition coextrudable with PVDF has now been found such that the UV stabilisers no longer exude, such that the PVDF/coextrudable composition two-layer film has good mechanical strength, which results in excellent adhesion of the PVDF layer to the substrate and which is resistant to radiation.

The present invention relates to a composition suitable as an adhesive layer coextrudable with PVDF and comprising:

- 20 to 40 parts of PVDF;
- 40 to 60 parts of PMMA;
- 5 to 18 parts of an acrylic elastomer;
- 1 to 4 parts of a UV absorber;
- the total making 100 parts.

Thus, the composition of the invention on the one hand can tolerate less than 50 parts by weight of PMMA and on the other hand the relationship among the components

is very different than the relationships in U.S.
5,242,976.

The invention also relates to coextruded films
5 comprising:

- a layer of the above coextrudable composition (also called adhesive layer) directly attached to the latter; and
- a PVDF-based layer comprising, as main constituents,
10 50 to 100 parts of PVDF per 50 to 0 parts of PMMA respectively (this layer is also called for simplification "PVDF layer").

According to a second form of the invention, the PVDF
15 layer is in the form of two layers:

- one placed against the coextrudable layer and comprising, as main constituents, 50 to 90 parts of PVDF per 50 to 10 parts of PMMA respectively; and
- the other (also called the outer layer) comprising,
20 as main constituents, 75 to 100 parts of PVDF per 25 to 0 parts of PMMA respectively.

These films possess mechanical properties sufficient to allow them to be handled to be processed and to be used
25 as a coating transparent to visible light but opaque to UV radiation.

The invention also relates to the substrates coated with this film, the coextrudable (adhesive) composition
30 being placed against the substrate.

With regard to PVDF, this term denotes PVDFs, vinylidene fluoride (VF2) homopolymers and vinylidene fluoride (VF2) copolymers preferably containing at
35 least 50% by weight of VF2 and at least one other monomer copolymerisable with VF2. Advantageously, the comonomer is fluorinated and may be chosen, for example, from the vinyl fluoride; trifluoroethylene (VF3); chlorotrifluoroethylene (CTFE); 1,2-difluoro-
40 ethylene; tetrafluoroethylene (TFE); hexafluoro-

propylene (HFP); perfluoro(alkyl)vinyl ethers, such as perfluoro(methyl)vinyl ether (PMVE), perfluoro(ethyl)vinyl ether (PEVE) and perfluoro(propyl)vinyl ether (PPVE); perfluoro(1,3-dioxole); perfluoro(2,2-dimethyl-1,3-dioxole) (PDD). Preferably, the possible comonomer is chosen from chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), trifluoroethylene (VF3) and tetrafluoroethylene (TFE).

Advantageously, the PVDF has a viscosity ranging from 100 Pa.s to 2000 Pa.s, the viscosity being measured at 230°C at a shear rate of 100 s⁻¹ using a capillary rheometer. This is because these PVDFs are well suited to extrusion and to injection moulding. Preferably, the PVDF has a viscosity ranging from 300 Pa.s to 1200 Pa.s, the viscosity being measured at 230°C at a shear rate of 100 s⁻¹ using a capillary rheometer.

With regard to PMMA, this term denotes methyl methacrylate homopolymers and copolymers containing at least 50% methyl methacrylate by weight. As examples of comonomers, mention may be made, for example, of alkyl(meth)acrylates, acrylonitrile, butadiene, styrene and isoprene. Examples of alkyl(meth)acrylates are described in Kirk-Othmer Encyclopaedia of Chemical Technology, 4th Edition in Vol. 1, pages 292-293 and in Vol. 16, pages 475-478. Advantageously, the PMMA may contain 0 to 20% and preferably 5 to 15% of methyl acrylate and/or ethyl acrylate by weight. The PMMA may be functionalised, that is to say it contains, for example, acid, acid chloride, alcohol or anhydride functional groups. These functional groups may be introduced by grafting or by copolymerisation. Advantageously, this is an acid functional group provided by the acrylic acid comonomer. Two neighbouring acrylic acid functional groups may lose water to form an anhydride. The proportion of functional groups may be between 0 and 15% by weight of the PMMA containing the optional functional groups.

The MVI (melt volume index) of the PMMA may be between 2 and 15 cm³/10 min measured at 230°C under a load of 3.8 kg.

5 With regard to the acrylic elastomer, this denotes any one of the following: Elastomers produced from monomers comprising acrylonitrile, for example, a copolymer of acrylonitrile and at least monomer chosen from butadiene, isoprene, alkyl (meth)acrylate and styrene.
10 Elastomers produced from monomers comprising alkyl(meth)acrylates, for example, copolymers of alkyl(meth)acrylate and at least one monomer chosen from butadiene, isoprene, acrylonitrile and styrene, and core-shell materials.

15 As regards a core-shell material, this is in the form of fine particles having an elastomer core and at least one thermoplastic shell, the size of the particles being in general less than 1 µm and advantageously
20 between 50 and 300 nm. The core-shell materials, because they contain at least 2 chemically different monomeric are referred to hereinafter as copolymers.

As an example of core materials, examples are isoprene
25 or butadiene homopolymers, isoprene copolymers with at most 30 mol% of a vinyl monomer and butadiene copolymers with at most 30 mol% of a vinyl monomer. The vinyl monomer may be styrene, an alkyl styrene, acrylonitrile or an alkyl(meth)acrylate. Another core
30 family consists of homopolymers of an alkyl(meth)-acrylate and copolymers of an alkyl(meth)acrylate with at most 30 mol% of a monomer chosen from another alkyl(meth)acrylate, and a vinyl monomer. Advantageously, the alkyl(meth)acrylate is butyl
35 acrylate. The vinyl monomer may be styrene, an alkyl styrene, acrylonitrile, butadiene or isoprene. The core of the core-shell copolymer may be completely or partly crosslinked. All that is required is to add at least difunctional monomers during preparation of the core,
40 it being possible for these monomers to be chosen from

poly(meth)acrylic esters of polyols such as butylene di(meth)acrylate and trimethylolpropane trimethacrylate. Other difunctional monomers are, for example, divinylbenzene, trivinylbenzene, vinyl acrylate and vinyl methacrylate. The core may also be crosslinked by introducing into it, by grafting or as comonomer during polymerisation, unsaturated functional monomers such as unsaturated carboxylic acid anhydrides, unsaturated carboxylic acids and unsaturated epoxides. For example, mention may be made of maleic anhydride, (meth)acrylic acid and glycidyl methacrylate.

The shell or shells are styrene, alkyl styrene or methyl methacrylate homopolymers or copolymers containing at least 70 mol% of one of these monomers mentioned above and at least one comonomer chosen from the other monomers mentioned above, another alkyl(meth)acrylate, vinyl acetate and acrylonitrile. The shell may be functionalised by introducing therein, by grafting or as comonomer during polymerisation, unsaturated functional monomers such as unsaturated carboxylic acid anhydrides, unsaturated carboxylic acids and unsaturated epoxides. As examples, mention may be made of maleic anhydride, (meth)acrylic acid and glycidyl methacrylate. Mention may be made, for example, of core-shell copolymers having a polystyrene core and core-shell copolymers having a PMMA shell. There are also core-shell copolymers having two shells, one made of polystyrene and the other on the outside made of PMMA. Examples of copolymers and their method of preparation are described in the following patents: US 4 180 494, US 3 808 180, US 4 096 202, US 4 260 693, US 3 287 443, US 3 657 391, US 4 299 928, US 3 985 704 and US 5 773 520.

Advantageously, the core represents 70 to 90% and the shell 30 to 10% by weight of the core-shell copolymer.

As an example of a copolymer, mention may be made of that comprises (i) of 75 to 80 parts of a core

comprising at least 93 mol% of butadiene, 5 mol% of styrene and 0.5 to 1 mol% of divinylbenzene and (ii) 25 to 20 parts of two shells essentially of the same weight, the inner one made of polystyrene and the other
5 outer one made of PMMA.

As another example, mention may be made of those having a poly(butyl acrylate) or butyl acrylate/butadiene copolymer core and a PMMA shell.

10 All these core-shell copolymers are sometimes called soft/hard copolymers because of the elastomer core.

There are also other types of core-shell copolymers such as hard/soft/hard copolymers, that is to say they
15 have, in this order, a hard core, a soft shell and a hard shell. The hard parts may comprise the polymers of the shell of the above soft/hard copolymers and the soft part may comprise the polymers of the core of the above soft/hard copolymers. Non-limiting examples of
20 such core-shell polymers comprise in order:

- a core made of a methyl methacrylate/ethyl acrylate copolymer;
- a shell made of a butyl acrylate/styrene copolymer; and
- 25 • a core made of a methyl methacrylate/ethyl acrylate copolymer.

There are also other types of core-shell copolymers such as hard (core)/soft/semi-hard copolymers. Compared
30 with the previous ones, the difference stems from the "semi-hard" outer shell which comprises two shells, one being the intermediate shell and the other the outer shell. The intermediate shell is a copolymer of methyl methacrylate, styrene and at least one monomer chosen
35 from alkyl acrylates, butadiene and isoprene. The outer shell is a PMMA homopolymer or copolymer. Non-limiting examples of such copolymers comprise in order:

- a core made of a methyl methacrylate/ethyl acrylate copolymer;
- 40 • a shell made of a butyl acrylate/styrene copolymer;

- a shell made of a methyl methacrylate/butyl acrylate/styrene copolymer; and
- a shell made of a methyl methacrylate/ethyl acrylate copolymer.

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When choosing the proportions of acrylic elastomer, it is necessary to take into account that which may already be contained in the PMMA. This is because there are commercial grades of PMMA called "impact" grades which contain acrylic impact modifiers, usually of the core-shell type. These acrylic impact modifiers may also be present in the PMMA because they were introduced during its polymerisation or prepared simultaneously during its polymerisation.

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As regards the UV absorber, these are products known per se. Such products are cited in U.S. Patent 5,256,472. Advantageously, benzotriazoles and benzophenones are used. As an example, Tinuvin® 213 or Tinuvin® 109 and preferably Tinuvin® 234 from Ciba Specialty Chemicals may be used.

The composition coextrudable with PVDF advantageously comprises:

- 25 to 35 parts of PVDF;
- 45 to 55 parts of PMMA;
- 8 to 18 parts of an acrylic elastomer;
- 2 to 3 parts of a UV absorber;
- the total making 100 parts.

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The composition coextrudable with PVDF preferably comprises:

- 30 to 35 parts of PVDF;
- 50 to 55 parts of PMMA;
- 8 to 12 parts of an acrylic elastomer;
- 2 to 3 parts of a UV absorber;
- the total making 100 parts.

The coextrudable composition may be prepared by melt blending the PVDF, the PMMA and the acrylic elastomer

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to which the UV absorber is added. Advantageously, conventional thermoplastic mixers are used.

5 With regard to the coextruded film comprising the coextrudable composition and the PVDF layer, the thickness of the PVDF layer is advantageously between 2 and 50 μm and that of the coextrudable composition between 10 and 100 μm .

10 Advantageously, the PVDF base layer comprises, as main constituents, 70 to 100 parts of PVDF per 30 to 0 parts of PMMA respectively and preferably 75 to 85 parts of PVDF per 25 to 15 parts of PMMA respectively.

15 According to a second form of the invention, the PVDF layer is in the form of two layers: 2

- one placed against the coextrudable layer and comprising, as main constituents, 50 to 90 parts of PVDF per 50 to 10 parts of PMMA respectively; and
- 20 • the other (also called the outer layer) comprising, as main constituents, 75 to 100 parts of PVDF per 25 to 0 parts of PMMA respectively.

That is to say the films of the invention comprise, in
25 the following order:

- a coextrudable layer of the composition of the invention (the adhesive layer);
- a layer placed against the coextrudable layer and comprising, as main constituents, 50 to 90 parts of
30 PVDF per 50 to 10 parts of PMMA respectively; and
- a layer (also called the outer layer) comprising, as main constituents, 75 to 100 parts of PVDF per 25 to 0 parts of PMMA respectively.

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The outer layer advantageously comprises, as main constituents, 85 to 100 parts of PVDF per 15 to 0 parts of PMMA respectively and preferably 90 to 100 parts of PVDF per 10 to 0 parts of PMMA respectively.

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The thickness of the layer of coextrudable composition is advantageously between 10 and 100 μm and that of each of the other layers is advantageously between 2 and 50 μm .

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The invention also relates to the substrates coated with this film, the coextrudable composition being placed against the substrate.

10 **With regard to the substrate**, mention may be made, by way of example, of:

- chlorinated polymers: PVC, PVC plastic, chlorinated PE;
- polymers and copolymers containing styrene, such as
- 15 ABS, SAN, PS;
- saturated polyesters (PET, PBT, etc.) and copolyesters or blends, unsaturated polyester resins (SMC);
- epoxy and phenolic resins;
- ethylene/alkyl acrylate or ethylene/vinyl acetate
- 20 copolymers (e.g. EMA or EVA), which are functionalised or unfunctionalised;
- PAs (polyamides) and CoPAs (copolyamides), PEBA, polyesteramides and TPU (thermoplastic polyurethane);
- EVOH (ethylene/vinyl alcohol) copolymer;
- 25 • aluminium, steel or mixtures of metals;
- lignin-based composites;
- acrylic compounds (PMMA, etc.)
- glass;
- PVC and PU foams.

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In the above description, it is to be understood that the examples of various components are not intended to be limiting of the broad scope of the generically described components.

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Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific

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embodiments are, therefore, to be construed as merely

illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

In the foregoing and in the following examples, all
5 temperatures are set forth uncorrected in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

The following products were used:

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KYNAR® 720 : a PVDF homopolymer from Atofina having an MVI (Melt Volume Index) of 10 cm³/10 min (230°C, 5kg);

15 **KYNAR® 740** : a PVDF homopolymer from Atofina having an MVI (Melt Volume Index) of 1.1 cm³/10 min (230°C, 5kg);

ALTUGLAS® BS8 : a PMMA from Atoglas having an MVI of 4.5 cm³/10 min (230°C; 3.8 kg) in bead form containing 12% of a methyl acrylate comonomer;

20 **ALTOGLAS® V 825 T** : a PMMA from Atoglas having an MVI of 2.5 cm³/10 min (230°C; 3.8 kg);

TINUVIN® 109 : a UV absorber of the benzotriazole type sold by Ciba Specialty Chemicals;

25 **TINUVIN® 213** : a UV absorber of the (hydroxyphenyl) benzotriazole type sold by Ciba Specialty Chemicals;

TINUVIN® 234 : a UV absorber of the (hydroxyphenyl) benzotriazole type sold by Ciba Specialty Chemicals;

30 **D320** : the abbreviation for **DURASTRENGTH® D320**, denoting a soft/hard core-shell elastomer whose core is a butyl acrylate/butadiene copolymer and whose shell is made of PMMA, 80 nm in size, sold by CECA;

35 **PARALOID® KM 355** : denoting a soft/hard core-shell elastomer whose core is a butyl acrylate homopolymer and whose shell is made of PMMA, 150 nm in size, sold by Rohm and Haas.

Example 1 (according to the invention)

A two-layer film containing a layer composed of 80% KYNAR 720 PVDF and 20% ALTUGLAS BS8, 15 µm in thickness, and a binder 35 µm in thickness according to the following formulation: 31.8% KYNAR 720, 51.7% ALTUGLAS BS8, 2.5% TINUVIN 234 and 15% D320, this film having an elongation at break of 197%, a haze of 14 and, after seven days spent in an oven, no exudation being observable. This film has a UV absorbance sufficient for its use in outdoor applications.

10 Example 2: (according to the invention)

A two-layer film containing a layer composed of 80% KYNAR 720 PVDF and 20% ALTUGLAS BS8, 15 µm in thickness, and a binder 35 µm in thickness according to the following formulation: 33.6% KYNAR 740, 53.9% ALTUGLAS BS8, 2.5% TINUVIN 234 and 10% D320, this film having an elongation at break of 210%, a haze of 11 and, after seven days spent in an oven, no exudation being observable. This film has a UV absorbance sufficient for its use in outdoor applications.

Example 3: (according to the invention)

A two-layer film containing a layer composed of 80% KYNAR 740 PVDF and 20% ALTUGLAS BS8, 15 µm in thickness, and a binder 35 µm in thickness according to the following formulation: 33.6% KYNAR 740, 53.9% ALTUGLAS BS8, 2.5% TINUVIN 109 and 10% D320, this film having an elongation at break of 150%, a haze of 8 and, after seven days spent in an oven, no exudation being observable. This film has a UV absorbance sufficient for its use in outdoor applications.

Example 4: (according to the invention)

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A two-layer film containing a layer composed of 80% KYNAR 740 PVDF and 20% ALTUGLAS BS8, 15 µm in thickness, and a binder 35 µm in thickness according to the following formulation: 33.6% KYNAR 740, 53.9% ALTUGLAS BS8, 2.5% TINUVIN 213 and 10% D320, this film

having an elongation at break of 150%, a haze of 6.5 and, after seven days spent in an oven, no exudation being observable. This film has a UV absorbance sufficient for its use in outdoor applications.

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Example 5: (according to the invention)

A two-layer film containing a layer composed of 80% KYNAR 740 PVDF and 20% ALTUGLAS BS8, 15 μ m in
10 thickness, and a binder 35 μ m in thickness according to the following formulation: 33.6% KYNAR 740, 53.9% ALTUGLAS BS8, 2.5% TINUVIN 234 and 10% D320, this film having an elongation at break of 150%, a haze of 6.5 and, after seven days spent in an oven, no exudation
15 being observable. This film has a UV absorbance sufficient for its use in outdoor applications.

Example 6 (comparative example)

20 A two-layer film containing a layer composed of 80% KYNAR 720 PVDF and 20% ALTUGLAS V825T, 15 μ m in thickness, and a binder 35 μ m in thickness according to the following formulation: 32.5% KYNAR 720, 32.5% ALTUGLAS V825T, 2.5% TINUVIN 234 and 32.5% PARALOID KM
25 355, this film having an elongation at break of 150%, a haze of 15 and, after one day spent in an oven, exudation being observable. This film has a UV absorbance insufficient for its use in outdoor applications.

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Example 7 (comparative example)

A two-layer film containing a layer composed of 80% KYNAR 720 PVDF and 20% ALTUGLAS V825T, 15 μ m in
35 thickness, and a binder 35 μ m in thickness according to the following formulation: 32.5% KYNAR 720, 32.5% ALTUGLAS V825T, 2.5% TINUVIN 234 and 32.5% DURASTRENGTH D320, this film having an elongation at break of 150%, a haze of 15 and, after one day spent in an oven,
40 exudation being observable. This film has a UV

absorbance insufficient for its use in outdoor applications.

5 The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

10 The entire disclosures of all applications, patents and publications, cited herein and of corresponding French application No. 02.09024, filed July 17, 2002, and French application No. 02.11991, filed September 27, 2002 are incorporated by reference herein.

15 From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various
20 usages and conditions.